ACTIVATION OF METHANE BY TRANSITION METAL-SUBSTITUTED ALUMINOPHOSPHATE MOLECULAR SIEVES

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ABSTRACT

Recent experiments in our laboratory have demonstrated that aluminophosphate molecular sieves substituted with cobalt and cobalt/silicon combinations and having the $AlPO_4$-34 or $AlPO_4$-5 structure activate methane starting at ~350°C. Between 400 and 500°C the rate of methane conversion increases steadily with typical conversion efficiencies at 500°C ranging from 15 to 60%. The cobalt and silicon substituted $AlPO_4$-34 structure (CoAPSO-34) produces ethylene, ethane, propylene, and propane in varying proportions, depending on reaction conditions. The cobalt-substituted $AlPO_4$-5 (CoAPSO-5) produces propylene in very high yield, with ethane, ethylene, and propane also seen. Analogous aluminophosphate molecular sieves substituted with magnesium or silicon, but containing no transition metal (e.g., SAPO-34, MAPO-5), do not activate methane under the conditions described above. The activation mechanism is based on reduction of the cobalt(III) form of the molecular sieve to the cobalt(II) form with accompanying oxidative dehydrogenation of the methane. Reoxidation of the cobalt(II) form to the cobalt(III) form can be done either chemically (e.g., using O_2) or electrochemically.

INTRODUCTION

In a recently published paper (1) we reported the finding that when Co(II) is substituted for Al(III) in the framework of certain aluminophosphate ($AlPO_4$) molecular sieves and the resulting Co(II)-containing $AlPO_4$ (CoAPO) is calcined in oxygen, the Co(II) is oxidized to Co(III). Further work with these Co(III)APOs showed that they possess strong oxidizing capabillity, and, for example, can convert methanol to formaldehyde (at 25°C), NO to NO^+ (at 25°C), and H_2 to $2H^+$ (at ≥300°C). These results inspired the thought that Co(III)APOs might actually oxidize methane and in the process convert the activated species directly to light hydrocarbons by virtue of their known Bronsted acid catalyzed homologation capacity (2,3) and the product selectivity constraints imposed by their pore dimensions. Recent experiments in our laboratory (summarized below) have demonstrated that this is in fact the case.

EXPERIMENTAL

The synthesis methods used to prepare the aluminophosphate molecular sieve materials employed in this work have been discussed elsewhere (1). Reactions of methane on these molecular sieve materials and on several other metal oxides known to activate methane (e.g., Sm_2O_3) were carried out in a quartz tube reactor having an 8 mm inside diameter. The catalyst sample (~1 gram) was supported on a quartz fritted disk fused into the midsection of the quartz tube. The tube was mounted in an electrically heater furnace (with the sample in the middle of the heated zone) and attached to the gas handling system. The gases used in the experiments [99.999% He, 10% CH_4 in Ar (C_{2+} hydrocarbons/CH_4 ≃ 0.002), and "zero" air, all supplied by Matheson Gas Products] were introduced at the bottom of the

reaction tube. A quartz-sheathed thermocouple was positioned inside the reaction tube just above the bed of catalyst material. Electrochemical activation was accomplished by inserting two coiled sections of platinum wire that were flattened to conform to the side wall of the reaction tube and then mounted in the tube so that they faced each other with a spacing of ~3 mm.

In a typical experiment with a molecular sieve material, the sieve sample was calcined in "zero" air at 550°C in the reaction tube to burn off any remaining template ions (for a fresh sample) or carbonaceous residues (for a used sample). This calcining restored the cobalt-containing molecular sieves to the Co(III) form as described previously (1). After calcining, the reaction tube was brought to the desired temperature and purged of residual oxygen with flowing helium, then ~10 cc (STP) of the 10% CH_4 in Ar mixture was introduced at a rate of ~0.5 cc/min. The reaction products, unreacted CH_4, and Ar coming out the top of the reaction tube were collected in a liquid nitrogen cooled loop. The loop was then isolated from the reaction tube and warmed up to room temperature; after which a gas sample was withdrawn through a septum port on the side of the loop (using a gas syringe) and injected into a gas chromatograph (GC) equipped with a flame ionization detector (FID). In some experiments injections were also made into a GC equipped with a thermal conductivity detector (TCD) to determine the amounts of H_2O, CO, and CO_2 that were produced relative to the amount of CH_4 reacted.

Electrochemical activation studies were performed using a constant voltage power supply. Potentials in the range from 3 to 10 V dc were applied across the two platinum wire electrodes (described above). Gas handling procedures employed in the presence of an applied potential were the same as those used on air calcined molecular sieve samples, except that the sieve sample was fully reduced (deactivated) with CH_4 between the calcining and helium purging steps. The voltage was applied during purging and maintained throughout the CH_4 introduction step.

RESULTS

Methane activation experiments were performed on the following aluminophosphate molecular sieve materials: CoAPSO-34 (P:Co:Si = 12:1:1.8), CoAPO-5 (P:Co = 24:1), MAPO-5 (P:Mg = 12:1), and SAPO-34 (P:Si = 6.7:1). The onset temperature for activation of CH_4 by the cobalt-containing $AlPO_4$ (i.e., where a few percent of C_{2+} products are observed relative to the CH_4) occurs in the 350 to 400°C range. At 500°C the reaction proceeds more rapidly, and single pass conversions of CH_4 to C_{2+} hydrocarbons ranging from 15 to 30% have been observed. In single pass experiments without electrochemical stimulation, ~1 cc (STP) of methane deactivates almost all of the active sites in ~1 gram of the CoAPSO-34 or CoAPO-5, and recalcination with O_2 is required to reactivate the sieve material. Many air calcinings have been run on some samples of CoAPSO-34 without evidence of significant permanent loss of activity, but in most other cases we have observed steady decreases in activity with extended use. In the presence of applied dc potentials in the 3 to 10 V range, it is possible to activate the reduced form of the cobalt-containing molecular sieves [(HCo(II)APSO-34 and HCo(II)APO-5)] and achieve significant ($\geq$ 15%) methane conversion to C_{2+} hydrocarbons in a single pass at 500°C. However, even electrochemically activated samples tend to exhibit reduced activity with extended use.

Identical experiments were performed on the silicon-substituted $AlPO_4$-34 (SAPO-34) and magnesium-substituted $AlPO_4$-5 (MAPO-5), wherein air calcination and electrochemical stimulation were employed in the same manner as was used with the CoAPSO-34 and CoAPO-5. None of these experiments gave any evidence of methane activation to C_{2+} hydrocarbons. A test of air-calcined Sm_2O_3, a known methane

activation catalyst at ≥700°C (4), failed to produce any C_{2+} products in our apparatus for temperatures up to 580°C, using methane only as a reactant (no oxygen co-feed).

A summary of typical results from the experiments described above is given in Table I. Reproductions of FID gas chromatograms for the products of methane activation over an air calcined sample of CoAPSO-34, an electrochemically stimulated sample of CoAPSO-34, and an electrochemically stimulated sample of CoAPO-5 are shown in Figs. 1, 2a, and 2b, respectively. TCD gas chromatograms run on products from experiments where high yields of C_{2+} hydrocarbon were obtained typically showed relatively low levels of CO_2 (a few percent at most) and hardly any CO. If care was not taken to remove oxygen (as O_2) from the reaction environment prior to introduction of the methane, higher levels of CO_2 and lower levels of C_{2+} hydrocarbons were normally observed, i.e., the yields of C_{2+} hydrocarbons and CO_x have tended to be inversely related to one another in the types of experiments described above.

Finally, we wish to note that electrochemical stimulation experiments done on samples of Co(II)-exchanged SAPO-34 (P:Co ≤12) and Co(II)-exchanged Y zeolite (Si:Co ~5) at 500°C (using the same conditions as for the CoAPSO-34 and CoAPO-5 experiments) produced smaller (but nonetheless measurable) yields of the same products observed for CoAPSO-34 (see Table I). In the case of single pass experiments with Co(II)-exchanged Y zeolite, evidence of a few percent conversion of methane to C_{2+} hydrocarbons at 500°C was also seen for a sieve sample that was air calcined at 550°C prior to methane exposure.

DISCUSSION

The results presented in the preceding section give clear evidence that cobalt-substituted aluminophosphate molecular sieves have the capability to catalyze the coupling of methane to C_{2+} hydrocarbons at temperatures ≤ 500°C. The single pass yields which have exceeded 30% at 500°C, the high selectivity to C_{2+} hydrocarbons, the encouraging observation that molecular oxygen is not essential to the activation process, and the absence of large quantities of CO_x in the product stream represent a significant advance in the state-of-the-art for methane coupling using inorganic catalyst materials. The further finding that the cobalt-substituted molecular sieve can be maintained in the active state by an electric field allows for the development of continuous methane homologation processes using, e.g., packed or fluidized electrochemical bed reactors.

Data from comparative experiments -- CoAPSO-34 vs SAPO-34 and CoAPO-5 vs MAPO-5 -- show that cobalt is essential to the activation process. Prior work (1) indicates that the active state of the cobalt is tetrahedrally-coordinated Co(III) bound in framework metal atom positions of the molecular sieve. The overall reaction mechanism is believed to include the following steps:

$$2CH_4 + 2Co(III)APO \rightarrow C_2H_6 + HCo(II)APO \quad [1]$$

$$C_2H_6 + 2Co(III)APO \rightarrow C_2H_4 + HCo(II)APO \quad [2]$$

$$2HCo(II)APO \xrightarrow[\text{electric field}]{O_2 \text{ or}} Co(III)APO + H_2O \text{ or } H_2. \quad [3]$$

The formation of C_3 hydrocarbons could occur from reaction of methyl radicals ($CH_3\bullet$) with ethylene or from Bronsted acid catalyzed reactions involving

ethylene. All of the above reactions are believed to take place within the molecular sieve framework which selectively constrains the size and shape of the transition state species and the products.

Although we assume that the framework-bound cobalt is the active agent in this catalysis, there was evidence that air calcined and electrochemically stimulated beds of Co(II)-exchanged SAPO-34 and Co(II)-exchanged Y zeolite also produced detectable quantities of C_{2+} hydrocarbons when exposed to methane at 500°C. This apparent catalytic activity of Co(II)-exchanged molecular sieves, which was actually predicted recently in the modeling work of Aparicio and Dumesic (5), is believed to occur by a mechanism that is separate from, but possibly related to, the one given above for framework-bound Co(II)/Co(III) in $AlPO_4$ molecular sieve structures.

The effectiveness of electrochemical stimulation as a redox activator was not unexpected in this work. There is increasing evidence (6) that molecular sieve materials are good ionic conductors at elevated temperature and have great potential for use in gas phase electrocatalysis applications. Also, Creasy and Shaw (7) recently demonstrated the electrocatalytic activity of CoAPSO-34 microelectrodes in the presence of methane using cyclic voltammetry.

There are a number of aspects of the research findings described above that call for further, more detailed study. Other transition metals, such as manganese and iron, can be substituted into the framework of $AlPO_4$ molecular sieves (2,3) and these might also exhibit methane coupling activity. The fact that a variety of pore sizes and framework architectures are possible with $AlPO_4$ molecular sieves (2,3) should be exploited to determine the relationship between sieving properties and activity/selectivity. The optimum amount of transition metal substitution, the role (beneficial or otherwise) of non-redox type acid site creators (e.g., Si, Mg, Zn) in the framework, and the optimum balance between redox and non-redox framework metal atoms requires exploration. Factors such as framework demetalization, over-dehydrogenation (leading to soot formation), the need for oxygen potential control (to avoid destabilization of the framework structure), and the role of impurities (e.g., H_2O) in the activation and ionic conduction processes all need to be elucidated. Foremost among the concerns stemming from our research to date are the causes of the gradual loss of catalytic activity observed for the CoAPSO-34 and CoAPO-5 sieve materials, and the implicit need for a methodology to identify/produce more stable, resilient transition metal-substituted $AlPO_4$ structures.

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Table I. Examples of Product Distributions from Typical[a] Methane Activation Experiments at 500°C

Molecular Sieve	Activation Method	Number of Passes	Product Distribution (Mole %) CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6
CoAPSO-34	Air calcine	Single	65	15	12	1	7
	Electrochem.	Single	91	5	1	2	1
	Electrochem.	Multiple[b]	85	4	3	4	4
SAPO-34	Air Calcine	Single	99	nil			
	Electrochem.	Single	99	nil			
CoAPO-5	Air Calcine	Single	54	1	5	1	39
	Air Calcine	Multiple[b]	21	1	10	1	67
	Electrochem.	Single	58	2	4	4	32
MAPO-5	Air Calcine	Single	99	nil			
	Electrochem.	Single	99	nil			
Co(II)-EX[c] SAPO-34	Electrochem.	Single	98[d]	0.5	0.4	0.3	0.3
Co(II)-EX[c] Y Zeolite	Electrochem.	Single	98	1	1	-	-
	Electrochem.	Multiple[b]	94	1	1	1	3

(a) The data presented in this table were derived from averages of several of the better results obtained with each material.

(b) In multiple pass experiments the unreacted methane and products from the first pass are recycled through the bed four or five additional times.

(c) Indicates Co(II) exchanged molecular sieve material.

(d) A fifth undetermined low molecular weight product was observed with Co(II)-exchanged SAPO-34. It was not acetylene, cyclopropane, or CO.

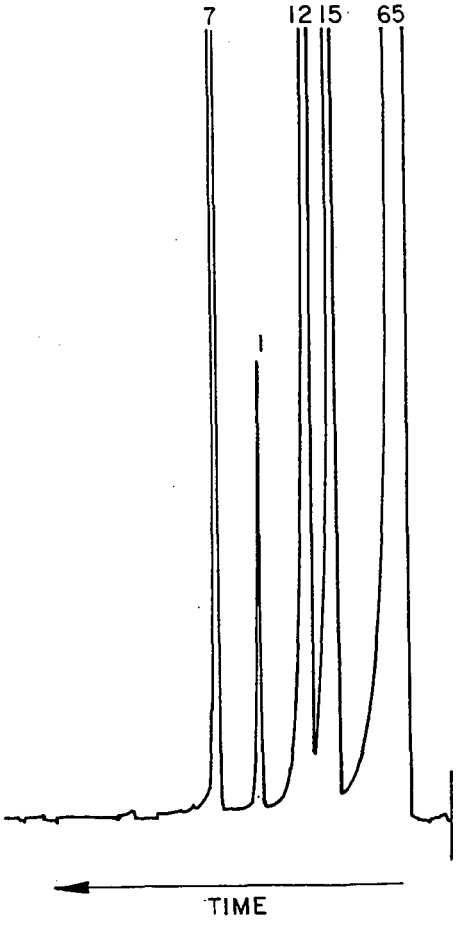

Figure 1. Gas chromatogram of the products from a typical single pass reaction of methane over air calcined CoAPSO-34 at 500°C. The numbers above each peak give the approximate mole percentages of each gas, i.e., 65% = CH_4, 15% = C_2H_6, 12% = C_2H_4, 1% = C_3H_8, and 7% = C_3H_6.

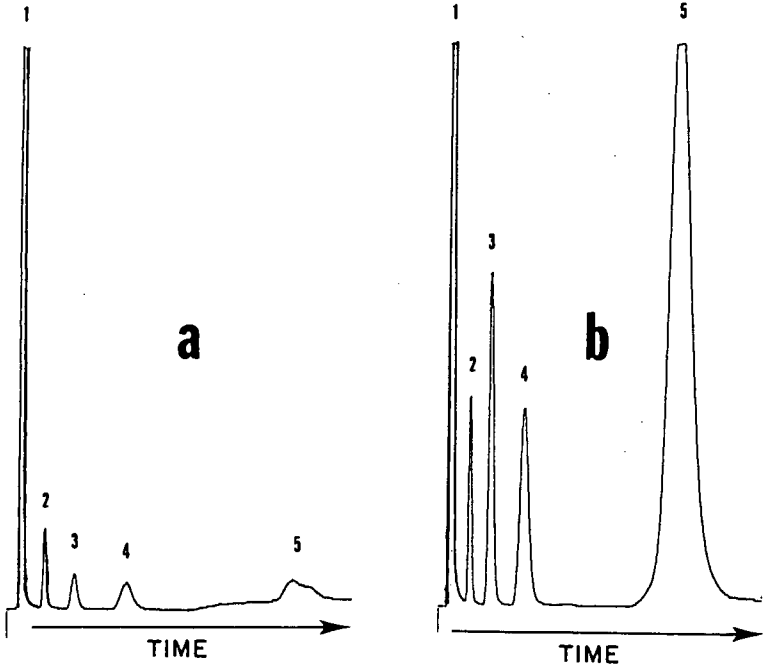

Figure 2. Results of single pass reactions of methane over electrochemically stimulated (10 V) CoAPSO-34 (insert a) and CoAPO-5 (insert b) at 500°C. Peaks 1 through 5 are CH_4, C_2H_6, C_2H_4, C_3H_8, and C_3H_6, respectively.